Cr-Al-steel for high temperature applications.

The present invention relates to a product of ferritic stainless steel manufactured according to the process of this invention, which product has increased resistance to cyclic and continuous thermal load and oxidation at increased temperatures and which has improved mechanical properties at said temperatures as well as the use thereof in the form of wire, strip, foil and/or tube in high-temperature applications such as in catalytic converter applications, in heating and furnace applications.

Background

Fe-Cr-Al-alloys have extensive use in the temperature range above 900 °C. Thanks to the protective oxide on the surface, they resist cyclic and continuous thermal load and oxidation until the material is depleted of the oxide former, e.g., Al. The limiting factors for the manufacture and the service life of the entire device are the total content of Al and the mechanical strength.

Description of Prior Art

Metallic high-temperature materials in, for instance, catalytic converters or for applications for resistive heating are today normally based on thin strips or wire of ferritic Fe-Cr-Al-alloys having at least 4,5 % of Al and small amounts of reactive elements added. The high ductility of the metal gives a good resistance to mechanical and thermal fatigue. Aluminium in contents above approx. 4,5 % by weight, together with the reactive elements, imparts the material the possibility of forming a thin, protective aluminium oxide upon heating. Furthermore, the reactive elements cause that the oxide gets a considerably reduced tendency of peeling or flaking, i.e., to come loose from the metal upon cooling or mechanical deformation. Conventional Fe-Cr-Al-alloys have, however, a great disadvan-

tage: they are mechanically very weak at high temperature, and tend, therefore, to be considerably deformed also at small stresses by virtue of, e.g., acceleration, changes of pressure, mechanical impacts or changes of temperature. The alloy disclosed in EP-B-290 719, which is intended for use in the manufacture of heating elements for resistive heating of furnaces etc., as well as construction parts in catalytic converters, solves the problem of decreasing the elongation of the substrate material in relation to the protective the oxide layer as a consequence of the combined effect of addition of Ti and Zr to the alloy.

Ferritic steel materials having low content of carbon are also embrittled by grain growth upon use in temperatures above 800 °C. The low content of carbon is required in order to obtain an optimal oxidation resistance of the alloy and enable plastic cold working since contents of carbon above approx. 0,02 % by weight have an embrittling effect by increasing the brittle transition temperature of the material. Elements that are used for solid solution hardening of high-temperature materials, such as Mo and/or W, are regarded to have a considerable negative impact on the oxidation properties, and therefore the desirable content of these elements may be limited to at most 1 % such as in US 4859649 or at most 0,10 % as in EP 0667400.

Summary

Therefore, it is an object of the present invention to provide an alloy of a ferritic stainless steel having elevated resistance to cyclic and continuous thermal load and oxidation at elevated temperatures.

It is an additional object of the present invention to provide a ferritic stainless steel that has improved mechanical properties for the use in applications with cyclic and continuous thermal load and oxidation at elevated temperatures such as, e.g., supporting material in converter applications, such as catalysts.

It is an additional object of the present invention to provide a ferritic stainless steel for the use in heating applications and in furnace applications.

It is an additional object of the present invention to provide a ferritic stainless steel in the form of wire, strip, foil and/or tube.

It is an additional object of the present invention to provide a process for the manufacture of a product of said alloy.

Description of the Figures

Figure 1 shows results of the oxidation testing at 1000 °C as a function of the change of mass versus time for examples D and E as well as comparative examples 1 and 3.

Figure 2 shows results of the oxidation testing at 1100 °C as a function of the change of mass versus time for examples C, E and G as well as comparative example 1.

Description of the invention

These objects are met by means of a ferritic stainless steel having the following composition (in % by weight):

less than 1 % of Ni,
15–25 % of Cr,
4,5–12 % of Al,
0,5–4 % of Mo,
0,01–1,2 % of Nb,
0–0,5 % of Ti,
0–0,5 % of Y, Sc, Zr and/or Hf,

0–0,2 % of one or more rare earth metals (REM) such as, for instance, Ce or La,
0–0,2 % of C,
0–0,2 % of N,
with the balance iron and normally occurring impurities.

The final product may be manufactured in the form of wire, strip, foil and/or tube.

The final product according to the present invention is manufactured as a homogeneous material or a laminate or a material having a concentration gradient of Al, where the content of Al increases toward said surface of the product. Thus, the manufacture may be effected by coating a substrate material and a substrate alloy, respectively, with Al or an alloy of Al, especially by coating strips of a substrate alloy of a thickness below 1 mm with an alloy of Al.

By this two-step process, the mechanical properties and oxidation resistance of the alloy can be improved and optimized independently of each other. This process also enables a simplification of the production process when manufacture via conventional pyrometallurgy of materials having average contents of Al above the average above 4,5 % is associated with great yield losses by virtue of brittleness. An additional advantage of this process is that a final material may be manufactured having a gradient of Al, such that the content of Al increases toward the surface, which entails improved oxidation resistance since the formation of fast growing oxides such as chromium and iron oxides is prevented and the mechanical properties of the final material are improved.

The substrate alloy may be manufactured by conventional pyrometallurgy or, for instance, powder metallurgy with the intended composition, and then the alloy is hot- and cold-rolled to final desired dimension.

In production by a coating process, before the coating the substrate material has the following composition (in % by weight):

less than 1 % of Ni,
15–27 % of Cr,
0–5 % of Al,
0,5–5 % of Mo,
0,01–2 % of Nb,
0–0,5 % of Ti,
0–0,5 % of Y, Sc, Zr and/or Hf,
0–0,2 % of one or more rare earth metals (REM) such as, for instance, Ce or La,
0–0,2 % of C,
0–0,2 % of N,
with the balance iron and normally occurring impurities.

The most suitable composition of the substrate material is the following (in % by weight):

less than 1 % of Ni,
16–25 % of Cr,
0,5–4 % of Al,
0,7–4 % of Mo,
0,25–1,0 % of Nb,
0–0,5 % of Y, Sc, Zr and/or Hf,
0–0,5 % of Ti,
0–0,1 % of one or more rare earth metals (REM) such as, for instance, Ce or La,
0,02–0,2 % of C,
0–0,05 % of N,
with the balance iron and normally occurring impurities.

The material may be used in the as coated condition or after a diffusion-annealing. The most favourable compositions of the substrate material before

coating are obtained if it contains 2–4 % of Al. This aluminium content imparts the final product an increased oxidation resistance and results in a simplified production process, i.e., the risk of production disturbances in comparison with the manufacture of a material having a aluminium content above 4 % is considerably decreased. After coating with alloy of Al, the material should in total contain a content of Al that is greater than 4,5 % by weight.

Mechanical stability and resistance to grain growth are provided by the presence of precipitations of carbides and/or nitrides of one or some of the elements Ti, Nb, Zr, Hf. Increased strength at high temperatures, i.e., temperatures above approx. 800 °C is also provided by the presence of Mo and/or W in solid solution. In the alloy according to the present invention, Mo may entirely or partly be replaced by W with a maintained effect on the alloy.

Addition of Zr and/or Hf and REM and/or Y and/or Sc provides an increased resistance to peeling and flaking of the formed oxide. The contents of the final product of the same elements may be supplied by adding these in the substrate alloy and/or in the alloy of Al that is used in the coating. The alloy according to the present invention should totally contain at least 0,1 % by weight of Ti+Nb+Zr+Hf.

Most compositions of the alloy according to the invention can be manufactured by conventional metallurgy. However, by the two-step process according to the present invention, a material is obtained the microstructure of which is controlled, the oxidation properties of which are improved, the mechanical properties of which are optimised and improved, and the maximum aluminium content of which is not limited by the embrittling effect that contents of Al above approx. 5 % by weight normally may give, both upon cold and hot working. Furthermore, the process to coat a substrate material with an alloy of Al provides a finished product the contents of which of, e.g., Mo, Nb and C can be considerably higher than in a conventionally manufactured material without the presence of these elements resulting in any noticeable deterioration of the oxidation properties.

Coating of the substrate alloy with alloy of Al may be effected by previously known processes such as, for instance, dipping in melt, electrolytic coating, rolling together of strips of the substrate alloy and the aluminium alloy, deposition of solid alloy of Al from a gas phase by so-called CVD or PVD technique. The coating with alloy of Al may be effected after the substrate alloy having been rolled down to desired final thickness of the product, or in larger thickness. In the latter case, a diffusion-annealing may be carried out in order to achieve a homogenization of the material, and then rolling in one or more steps is carried out in order to provide the finished product. Rolling may also be effected directly on a coated product according to the present invention having greater thickness than the desired final thickness. In this case, the rolling may be followed by annealing.

The thickness of the coated layer of Al may be varied depending on the thickness of the substrate material, the desired aluminium content in the final product and the aluminium content in the substrate material. However, the total content of Al in the finished product has to, as has been mentioned above, always be at least 4,5 % by weight. The product may be used in the form of an annealed, homogeneous material or a laminate or a material having a concentration gradient of Al where the content of Al is higher at the surface than in the centre of the material. For a material having a concentration gradient, a lower total content and average content down to 4,0 % by weight, respectively, can be allowed if the aluminium content at a distance of at most 5 µm from the surface is more than 6,0 % by weight.

Examples of useful aluminium alloys are pure Al, Al alloyed with 0,5–25 % by weight of Si, Al alloyed with 0–2 % by weight of one or more of the elements Ce, La, Y, Zr, Hf. Depending on the coating process used, different compositions of the alloy of Al are more suitable than others. Thus, it is, upon coating from melt, desirable that the melting point is low and that a homogeneous material or a eutectic mixture is deposited. Upon coating by rolling-on, it is required

that the material is ductile and has similar mechanical properties as the substrate so that coating and substrate are deformed in the similar way.

Example 1

Table 1 shows compositions of examined alloys. Example C and comparative example 1 were prepared in the conventional way by pyrometallurgy and hot working. From comparative example 1, 50 µm thick strips were also prepared via hot rolling and cold rolling. Comparative example 1 is an alloy that today is used as supporting material in catalytic converters. This material has sufficient oxidation resistance for this use. However, the mechanical strength thereof is low and is regarded to be the limiting factor of the service life of the entire device.

The very low ductility at room temperature (2 % elongation at fracture) of the alloy according to example C entails that this alloy hardly can be manufactured in the form of thin strips. However, the same alloy has, as is seen in table 1, a very good high temperature strength, thus at 700° and 900 °C the ultimate strength, for instance, is approx. 100 % higher than for comparative example 1. The oxidation resistance of example C and comparative example 1 at 1100 °C is shown in figure 2. The oxidation rate of example C is 5 % higher than of comparative example 1, which means that the materials can be considered as equivalents as regards oxidation resistance.

Example 2

Table 1 shows compositions of examined alloys. Examples A and B and comparative examples 1 and 2 were prepared in the conventional way by pyrometallurgy and hot working. Then 50 µm thick strips of all alloys were also prepared via hot rolling and cold rolling. The alloys according to examples A and B are all

sufficiently ductile at room temperature in order to be able to be cold-rolled to very thin strips of good productivity.

Examples D and E and comparative example 3 correspond to cold-rolled strips of alloy according to examples B and C and comparative example 2, respectively, which was coated by vaporization or sputtering with Al on both sides in such a quantity that the total content of Al corresponded to 5,5–6 % (see table 3).

Table 3

Example	Substrate alloy	Thick-ness before coating [μm]	Coated thickness of coated Al alloy [μm]	Desired total content of Al [%]	Measured coating thickness [μm]
D	A	50	5	6	
E	B	50	4	6	4,1
Comparative example 3	Cf. example 2	50	5	6	4,7

The obtained thickness of Al was measured by means of GDOES (glow discharge optical emission spectroscopy), a method that enables accurate measuring of compositions and thicknesses of thin surface layers. The analyses showed that a total content of Al of 5–6 % had been attained. These samples were oxidized in air at 1000 °C for up to 620 h, which is shown in figure 1. The alloys according to examples D and E are superior to the alloy according to comparative example 3, while the conventionally manufactured alloy of Fe-Cr-Al in comparative example 1 has a significantly better oxidation resistance than examples D and E of the alloy according to the invention.

Example 3

Examples F and G and comparative example 4 have the same composition as the alloys according to examples D and E and comparative example 3 having been annealed at 1050 °C for 10 min with the purpose of providing an

equalising of the content of Al in the material. The ductility of the material was determined by a bending test where the smallest bending radius that the material could be bent to without fracture was determined, see table 4.

Table 4

Example	Composition	Diffusion annealing in H_2 [min/1050 °C]	Smallest bending radius without fracture [mm]	Results of tensile testing at 900 °C [Rm/MPa]
F	The same as example D	10	0,5	46
G	The same as example E	10	0,38	81
Comparative example 4	The same as comparative example 3	10	2,5	could not be measured due to brittleness

The smallest radius that the material was tested at was 0,38 mm. The alloys according to the invention have a ductility being superior to comparative example 4. The alloy according to comparative example 4 proved to be so brittle that this alloy has to be regarded as less suitable for the use in catalytic converters. The alloy according to example G has an ultimate strength at 900 °C that is equally good as the conventionally manufactured material according to the invention, example C, and twice as high as the conventionally manufactured alloy of Fe-Cr-Al in comparative example 1. This means that, upon the assumption that the oxidation resistance is sufficient, this alloy can be used in a thickness that is half of the thickness of a conventional material, and thereby enable an increase in efficiency and a reduction of the material cost for the manufacture of catalytic converters.

The alloy according to example G was oxidation tested at 1100 °C together with the alloy according to examples C and E as well as comparative example 1, which is shown in figure 2. An improved oxidation resistance is obtained with the alloy according to example G, both by comparison with the same material without diffusion-annealing (example E) and with conventionally manufactured

alloys. The comparison between example G and example C is especially interesting, since these correspond to alloys having very similar composition but different ways of production: the alloy according to example G is prepared by cold rolling to desired thickness, followed by Al coating and annealing while example C has been prepared with desired content of Al in the alloy from the beginning. Apart from the improved production properties of a material that has been prepared in the way of example G, in addition this alloy has a better oxidation resistance than example C. The relatively seen lower oxidation resistance that example C has in comparison with comparative example 1 may be explained by a negative effect on the oxidation resistance by virtue of the presence of Mo and Nb in the alloy according to example C. It is known that these elements may deteriorate the oxidation resistance of an alloy. In example G, these negative effects are absent, which may be interpreted as a positive result of example G having been prepared by Al-coating. Thus, this method of manufacture is favourable as regards the oxidation resistance of the alloy.

To sum up, it may be observed that by the combined effect of high contents of Mo and Nb, a considerable improvement in the strength is provided in comparison with the material that is used today as well as that by using the described process, this material may be imparted the oxidation resistance required upon use at high temperatures of materials in weak dimensions and the above mentioned product forms.

The product of ferritic stainless steel manufactured according to the process of this invention has increased resistance to cyclic and continuous thermal load and oxidation at elevated temperatures and has improved mechanical properties at said temperatures, which makes it suitable for use in high-temperature applications such as in catalytic converter applications and in heating and furnace applications in the form of wire, strip, foil and/or tube.

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Table 1

Example	C	N	Ni	Al	Cr	Nb	Mo	Zr	REM	Ti	Si	Mn
A	0,007	0,074	0,10	<0,01	22,23	0,73	1,05	0,065		0,036	0,10	0,13
B	0,097	0,032	0,08	0,83	22,11	0,77	2,02	0,002	0,009	0,12	0,11	0,11
C	0,099	0,043	0,08	4,9	21,87	0,79	2,00	0,002	0,11	0,12	0,11	0,12
Comparative example 1	0,01	0,01	0,3	5,3	20	0,01	0,01	0,01	0,03	0,01	0,3	0,3
Comparative example 2	0,100	0,034	3,12	<0,01	22,28	0,74	2,04	<0,01		0,049	0,12	0,12

Table 2

	Room temperature			700°C			900°C		
Example	Rp0,2	Rm	A5	Rp0,2	Rm	A5	Rp0,2	Rm	A5
A	359	470	26	150	165	29	40	59	67
B	442	561	22	145	172	58	51	73	80
C	514	579	2	234	267	46	48	84	110
Comparative example 1	480	670	25	50	140	90	20	40	150
Comparative example 2	555	614	9	148	168	56	42	67	91